

FLUORINE COMPOUNDS, INORGANIC, GERMANIUM

Germanium forms both a difluoride and a tetrafluoride. It also forms a stable hexafluorogermanate complex ion, GeF_6^{2-} , that is present in the aqueous acid and a number of salts.

1. Germanium Difluoride

Germanium difluoride [13940-63-1] is a white solid, mp 110°C, and $d_{23} = 3.7 \text{ g/cm}^3$. This compound can be vacuum distilled. In a mass spectrometer, ions corresponding to $(\text{GeF}_2)^+_n$, where $n = 1 - 4$ have been observed at 361–403 K (1). At higher temperatures, GeF_2 disproportionates to GeF_4 (g), Ge (s), and GeF (g). Presumably the GeF [39717-71-0] formed is unstable and subsequently condenses and disproportionates. The initially reported (2) orange-red solid becomes red-brown going finally to the black of metallic Ge. The difluoride deliquesces (2) in moist air producing germanium(II) hydroxide (see Germanium and germanium compounds). The difluoride is soluble in aqueous hydrofluoric acid and gives a solution having the reducing properties expected of divalent germanium. GeF_2 reacts with aqueous solutions of alkali metal fluorides to produce trifluorogermanites (3), eg, cesium trifluorogermanite [72121-41-6], CsGeF_3 , and potassium trifluorogermanite [7212142-7], KGeF_3 . The GeF_3^- ion is oxidized to GeF either by oxygen in neutral solution or by its reduction of H^+ to hydrogen in hydrofluoric acid solution. Germanium difluoride is soluble in ethanol (2), forms a reversible complex with diethyl ether (2), and forms a dimethyl sulfoxide complex [72121-40-5], $\text{GeF}_2 \cdot \text{OS}(\text{CH}_3)_2$, which is decomposed at 240°C (3).

Germanium difluoride can be prepared by reduction (2, 4) of GeF_4 by metallic germanium, by reaction (1) of stoichiometric amounts of Ge and HF in a sealed vessel at 225°C, by Ge powder and HgF_2 (5), and by GeS and PbF_2 (6). GeF_2 has been used in plasma chemical vapor deposition of amorphous film (see Plasma technology; Thin films) (7).

2. Germanium Tetrafluoride

Germanium tetrafluoride [7783-58-6] is a gas having a garlic-like odor, a reported (8) triple point of -15°C and 404.1 kPa (4.0 atm), and a vapor pressure near 100 kPa (ca 1 atm) at -36.5°C . Germanium tetrafluoride fumes strongly in air and is hydrolyzed in solution to form GeF_6^{2-} ions. Germanium tetrafluoride can be prepared (8, 9) by thermal decomposition of barium hexafluorogermanate [60897-63-4], BaGeF_6 . Direct fluorination of germanium has been reported to give GeF_4 of higher purity (2). High purity GeF_4 is also manufactured by reaction of a finely powdered GeO_2 suspension in H_2SO_4 with UF_6 (10) or by the reaction of Ge metal or its oxide with F_2 or NF_3 (11). COF_2 has been used as a mild fluorinating agent to produce GeF_4 from GeO_2 (12). GeF_4 is used in ion implantation (qv) in semiconductor chips (see Semiconductors) (13, 14). Germanium tetrafluoride acts as a Lewis acid (15, 16) to form complexes with many donor molecules. The tetrafluoride is commercially available.

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3. Fluorogermanates

Fluorogermanic acid [16950-43-9] solutions, H_2GeF_6 , are prepared by reaction of germanium dioxide and hydrofluoric acid or by hydrolysis of germanium tetrafluoride. Addition of potassium fluoride, barium chloride (9), or other salts results in hexafluorogermanates such as potassium hexafluorogermanate[7783-73-5], K_2GeF_6 , or BaGeF_6 , both of which are stable at temperatures up to 500°C where BaGeF_6 starts to decompose to GeF_4 and BaF_2 .

Germanium tetrafluoride produces hydrogen fluoride in aqueous acidic solutions. Hydrogen fluoride is toxic and very corrosive. The OSHA permissible exposure limit (17) and the American Conference of Governmental Industrial Hygienists' (ACGIH) TLV for fluoride is 2.5 mg/m^3 of air (18).

BIBLIOGRAPHY

"Germanium" under "Fluorine Compounds, Inorganic," in *ECT* 2nd ed., Vol. 9, pp. 584–585, by W. E. White, Ozark-Mahoning Co.; in *ECT* 3rd ed., Vol. 10, pp. 720–721, by C. B. Lindahl, Elf Atochem North America, Inc.

Cited Publications

1. K. F. Zmbov, J. W. Hastie, R. Hauge, and J. L. Margrave, *Inorg. Chem.* **7**, 608 (1968).
2. *Can. J. Chem.* **39**, 80 (1961).
3. E. L. Muettterties, *Inorg. Chem.* **1**, 342 (1962).
4. Jpn. Kokai Tokyo Koho 61111520 A2, (May 29, 1986), S. Ishihara, M. Hirooka, and S. Oono (to Showa).
5. P. Rivere, A. Castel, J. Stage, and C. Abdenhadheric, *Organometallics* **10**(5), 1227–1228 (1991).
6. S. M. Van der Kerk, *Polyhedron* **2**(6), 509–512 (1983).
7. EP 229707 A1 (July 22, 1987), S. Ishihara, M. Hirooka, J. Hanna, and I. Shimizu.
8. L. M. Dennis and A. W. Laubengayer, *Z. Phys. Chem.* **130**, 420 (1927).
9. C. J. Hoffman and J. S. Gutowsky, *Inorg. Syn.* **4**, 147 (1953).
10. Ger. Offen. DE 3841212 A1 (June 13, 1990), R. Doetzer.
11. EP 89-104364 (Mar. 11, 1989), I. Harada, Y. Yoda, N. Iwanaga, T. Nishitsuti, and A. Kikkawa.
12. S. P. Mallela, O. D. Gupta, and J. M. Shreeve, *Inorg. Chem.* **27**(1), 208–209 (1988).
13. A. Gottdang and co-workers, *Nucl. Instrum. Methods Phys. Res., Sect. B* **B55**(1–9), 310–313 (1991).
14. A. Ferreiro, J. DePontcharra, C. Jaussaud, and E. Lora-Tamayo, *Vacuum* **39**(7–8), 775–779 (1989).
15. E. L. Muettterties, *J. Am. Chem. Soc.* **82**, 1082 (1960).
16. R. C. Aggarwal and M. Onyszchuk, *J. Inorg. Nucl. Chem.* **30**, 3351 (1968).
17. *Code of Federal Regulation*, Title 29, Part 1910.1000, Washington, D.C., 1993.
18. *Threshold Limit Values for Chemical Substances and Physical Agents, 1992–1993*, The American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

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